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(54) Title: PREPARATION OF IONIC LIQUIDS

(57) Abstract: Provided is a method for preparation of non-halide based ionic liquids, comprising reacting a halide salt of an organic cation with a Bronsted acid in the presence of an alcohol or alkene or alkyne. The non-halide based ionic liquid product of the reaction can be purified by removing hydrocarbyl halide, and any unreacted starting materials and water if present, for example by distillation. The halide ion content of the ionic liquid product can be minimized by using an excess of alcohol or alkene or alkyne in the reaction and/or treating crude ionic liquid with a further quantity of alcohol or alkene or alkyne.

TITLE: PREPARATION OF IONIC LIQUIDS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of United States provisional patent application serial no. 60/339,468 filed December 14, 2001, entitled "METHOD FOR PRODUCTION OF IONIC LIQUIDS", which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION:

The present invention relates to the field of organic chemistry. In particular, the invention relates to the preparation of ionic liquids.

BACKGROUND OF THE INVENTION:

Low melting organic salts, also known as "ionic liquids", have found utility as solvents for example in organic synthesis, electrochemistry, and catalysis. They may also be used as phase-transfer catalysts, liquid-membrane materials, thermal transfer fluids, high temperature lubricants, plasticizers, in separation sciences, and as a component in electrical storage devices (such as electrochemical capacitors, batteries and fuel cells).

Ionic liquids provide an attractive potential alternative to traditional organic solvents for chemical reactions for many reasons. For industrial purposes, the low vapour pressure of ionic liquids is a very important feature. They are essentially non-volatile, a property that eliminates many of the containment problems typically encountered with traditional organic solvents. Since ionic liquids are often composed of poorly coordinating ions, they have the potential to provide a highly polar yet poorly coordinating solvent. Moreover, many of these solvents are immiscible with

traditional organic solvents and therefore provide a non-aqueous polar alternative to two-phase systems. Because of their distinctive solvent characteristics, they can be used to bring unusual combinations of reagents into the same phase. A recent review of the properties and uses of ionic liquids is provided in an article entitled "Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis," by Thomas Welton (Chem. Rev. 1999, 99, 2071-2083).

Non-halide based ionic liquids (i.e. ionic liquids having an anion other than a halide) can be prepared by metathesis of an organic halide salt with an alkaline metal non-halide salt or acid (see: Wilkes *et al.* (1992) *J. Chem. Soc. Chem. Comm.* 965; U.S. Patent No. 5,683,832; Bonhote *et al. Inorg. Chem* (1996) Vol. 35 (5), 1168-1178; U.S. Patent No. 5,827,602; U.S. Patent No. 5,182,405; WO 0016902; WO 0140146; WO 0187900; WO 0279212; and WO 0294883). However, conventional metathesis reactions have several drawbacks. For example, when carried out on a commercial scale, these reactions generate large quantities of organic and solid wastes. Also, conventional metathesis produces yields that are considerably less than 100%, more typically in the range 80-90%. These low yields are due at least in part to the fact that anion exchange readily establishes an equilibrium among the ions. Acid/base neutralization reactions can be used to prepare ionic liquids but this would require preparation of the phosphonium, imidazolium or ammonium hydroxides first. These are generally prepared from the corresponding halide.

Non-halide based ionic liquids prepared by conventional metathesis typically contain various contaminants, such as halide ions. For many purposes, the presence of halide ions is undesirable. For example, the

presence of halide ions may interfere with transition metal catalysts, such as palladium catalysts.

Halide ions and other contaminants are typically removed from ionic liquids produced by metathesis by washing with water, filtering and drying the ionic liquid. The additional purification steps reduce the overall economy of the process, generating aqueous waste that must be disposed of and reducing overall yield of ionic liquid product.

Further, available processes for preparing ionic liquids often use an excess of reagents such as alkaline metal salts, large quantities of water and organic solvents such as methylene chloride, acetone and acetonitrile.

There remains a need for more economical and efficient methods for preparing non-halide based ionic liquids on a commercial scale. There further remains a need for methods of preparing non-halide based ionic liquids that reduce the amount of halide ion present in the final product.

SUMMARY OF THE INVENTION:

The current invention provides a method for preparation of a compound of formula (I) Q^+A^-, the method comprising reacting:

(i) an organic halide salt of formula (II) Q^+X^-, wherein

Q^+ is an organic cation and

X^-, is a halide;

with

(ii) a Bronsted acid other than a hydrohalic acid, wherein said Bronsted acid has a conjugate base A^-; and

(iii) an alcohol or an alkene or an alkyne;

with the proviso that when Q^+ is 1-butyl-3-methylimidiazolium, the Bronsted acid is not H_2SO_4 or CH_3SO_3H.

For some purposes, the presence of halide ion in the product Q^+A^- is not of concern. However, for other purposes, the presence of halide ion in the product Q^+A^- is undesirable. The method may be used to obtain a product Q^+A^- that is completely or substantially free of halide, i.e. if it contains halide, the level of halide ion is sufficiently low that the halide ion does not interfere with the intended utility of the product Q^+A^-. For some halide-sensitive applications, compounds of formula (I) that contain small amounts of halide ions may be acceptable, for example in an amount ranging up to about 1000 parts per million (ppm), but preferably ranging up to only about 500 ppm, more preferably 300 ppm and even more preferably only up to 200 ppm. Desirably the amount of halide present in the product Q^+A^- does not produce detectable precipitate in a $AgNO_3$ test.

DETAILED DESCRIPTION:

In accordance with the present invention, a compound of formula (I) compound Q^+A^- is prepared by reacting (i) an organic halide salt (Q^+X^-) with (ii) a Bronsted acid other than a hydrohalic acid and having a conjugate base A^- and (iii) an alcohol or an alkene or an alkyne. This reaction also produces a hydrocarbyl halide and, when alcohol is used as a reagent, water.

Q^+X^- may be any organic halide salt, i.e. wherein X^- is fluoride, chloride, bromide, or iodine. Preferably, X^- is chloride or bromide.

Suitable cations for Q^+X^- include those that have at least one quaternary nitrogen atom or quaternary phosphorus atom having at least one hydrocarbyl group attached thereto, wherein the hydrocarbyl group is a C_1-C_{30} alkyl, C_1-C_{30} alkyloxy, C_3-C_7 cycloalkyl, C_3-C_7 cycloalkyloxy, C_6-C_{18} aryl, C_6-C_{18} aryloxy, C_7-C_{30} aralkyl, or C_7-C_{30} aralkyloxy. The hydrocarbyl group or groups present on the organic cation are preferably C_1-C_{14} alkyl groups, more preferably C_1-C_6 alkyl groups. When more than one hydrocarbyl group is present, the groups may be identical or different. The hydrocarbyl groups may be straight-chained or branched. Further, the hydrocarbyl groups may be substituted or unsubstituted or contain heteroatoms, provided that the substituents or heteroatoms do not interfere with the method of preparing Q^+A^-. Acceptable heteroatoms may include oxygen, silicon, and sulfur, and acceptable substituents include alkoxy, alkylthio, acetyl, and halogen atoms, such as fluorine. Suitable hydrocarbyl groups include: methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, sec-butyl, n-pentyl, iso-pentyl, 2-pentyl, n-hexyl, phenyl, octyl, decyl, undecyl, and tetradecyl. The quaternary nitrogen atom or quaternary phosphorus atom may be a ring-member in for example a five- or six-membered ring system containing one to five carbon atoms, unsubstituted or substituted for example with a hydroxy group or a hydrocarbyl group as described above, and optionally containing additional heteroatoms, such as nitrogen, oxygen and sulfur.

Thus, examples of organic halide salts for use in the current method include but are not limited to: ammonium salts, phosphonium salts, pyridinium salts, imidazolium salts, pyrazolium salts, pyrimidinium salts, pyridazinium salts, pyrazinium salts, triazolium salts (both 1,2,3-triazolium and 1,2,4-triazolium), tetrazolium salts, and

isothiazolium salts. Mention is made of the following organic halide salts: trihexyltetradecylphosphonium chloride; tetrabutylphosphonium bromide; tetraoctylphosphonium bromide; tetrapropylammonium bromide; tetrabutylammonium bromide; *N*-butylpyridinium bromide; 1-propyl-3-methylimidazolium bromide (pmim-Br); 1-butyl-3-ethylimidazolium bromide (beim-Br); 1-hexyl-3-ethylimidazolium bromide (heim-Br); 1-butyl-3-ethylimidazolium chloride (beim-Cl); and *N*-hexyl-3-picolinium bromide.

Some organic halide salts are commercially available. Alternatively, organic halide salts can be prepared by the reaction of an appropriate halogenoalkane with an appropriate nitrogen-containing or phosphorus-containing organic compound, such as an amine or phosphine.

HA may be any Bronsted acid (i.e. an acid having a proton and conjugate base) other than a hydrohalide. The conjugate base A^- of the Bronsted acid may be any anion other than a halide anion, including but not limited to: RSO_3^-, camphorsulfonates, RSO_2^-, RSO_4^-, $H_2PO_4^-$, $H_2PO_3^-$, $(RO)_2P(O)O^-$, $(R)P(O)(OH)O^-$, $(R)_2P(O)O^-$, RCO_2^-, NO_3^-, NO_2^-, ClO_4^-, phenolates, $HCrO_4^-$, $H_2AsO_4^-$, $H_2AsO_3^-$, $HSeO_3^-$, $HTeO_6^-$, and $HTeO_3^-$, wherein R is a hydrogen atom or a hydrocarbyl group. When Q^+ has a quaternary phosphorus atom or quaternary nitrogen atom, A^- can also be $(RSO_2)_2N^-$. Suitable R hydrocarbyl groups include: C_1-C_{30} alkyl, C_2-C_{30} alkynyl, C_2-C_{30} alkenyl, C_3-C_7 cycloalkyl, C_3-C_7 cycloalkenyl, C_6-C_{18} aryl, C_7-C_{30} aralkyl, C_8-C_{30} aralkenyl, or C_8-C_{30} aralkynyl. R may be substituted or unsubstituted or contain heteroatoms, provided that the substituents or heteroatoms do not interfere with the method of preparing Q^+A^-. Acceptable heteroatoms may include oxygen, nitrogen, silicon, and sulfur, and acceptable substituents include alkoxy, alkylthio, acetyl, and halogen atoms, such as fluorine. Examples of specific anions

include: $(CF_3SO_2)_2N^-$; $CF_3(CF_2)_2CO_2^-$; $CF_3(CF_2)_3SO_3^-$; $CH_3SO_3^-$; HSO_4^-; and $H_2PO_4^-$. Mention is made of the following non-limiting examples of Bronsted acids: methanesulfonic acid, bis(trifluoromethanesulfonyl)imide, DL-camphorsulfonic acid, sulfuric acid, benzoic acid, naphthoic acid, nitrobenzoic acid especially para-nitrobenzoic acid, chlorobenzoic acid especially ortho-chlorobenzoic acid, saturated fatty acids (such as palmitic acid) and unsaturated fatty acids (such as oleic acid).

If the Bronsted acid includes a group R that contains a hydroxyl or alkenyl or alkynyl moiety, the Bronsted acid itself may undergo halogenation, and it may therefore be unnecessary to add a further alcohol, alkene or alkyne reagent to react with halide. Of course, a further alcohol, alkene or alkyne can be added, if desired.

Water-sensitive anions are less suitable for use in reactions in the presence of an alcohol, where water is generated. Water-sensitive anions include aluminum (III) halides. Water-sensitive anions may be used for reactions involving alkenes and alkynes.

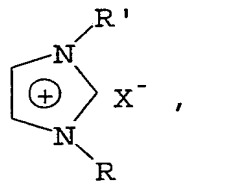
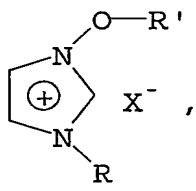
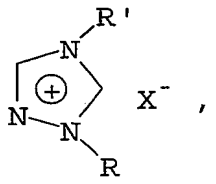
The alcohol may be a primary, secondary, or tertiary alcohol. Alcohols having between one and ten carbon atoms are preferred, with alcohols having between one and four carbon atoms being more preferred. Examples of alcohols include: methanol, ethanol, n-propanol, iso-propanol, n-butanol, sec-butanol, tert-butanol, pentanol, hexanol, heptanol, octanol, nonanol and decanol.

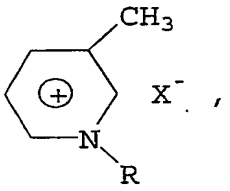
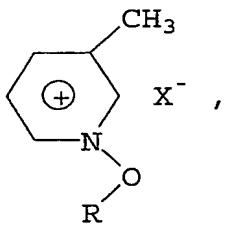
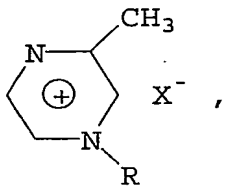
The alkene may be a C_2-C_{30} alkene, a C_3-C_7 cycloalkene, a (C_3-C_7 cycloalkenyl)C_1-C_{30} alkane, a (C_3-C_7 cycloalkane)C_2-C_{30} alkene, or a (C_6-C_{10}aryl)C_2-C_{30} alkene. C_2-C_{12} alkenes are preferred, and C_2-C_6 alkenes are more preferred. The alkene may be straight-chained or branched.

Examples of alkenes include: propene, butene, hexene, cyclopentene, and cyclohexene.

The alkyne may be a C_2-C_{30} alkyne, a (C_3-C_7 cycloalkyl)C_2-C_{30} alkyne, a (C_3-C_7 cycloalkenyl)C_2-C_{30} alkyne or a (C_6-C_{10} aryl)C_2-C_{30} alkyne. C_2-C_{12} alkynes are preferred, and C_2-C_6 alkynes are more preferred. The alkyne may be straight-chained or branched. Examples of alkynes include: acetylene, propyne, butyne, pentyne, hexyne.

Examples of compounds of formula (I) Q^+A^- include those represented by the following formulae:

$(R)_4N^+X^-$ and $(R)_4P^+X^-$,

wherein R and R′ are alkyl radicals with 1 to 12 carbon atoms, and

X- is $(CF_3SO_2)_2N$-, $CF_3(CF_2)_2CO_2^-$, $CF_3(CF_2)_3SO_3^-$, $CH_3SO_3^-$, HSO_4^-, or $H_2PO_4^-$.

Mention is made of the following compounds of formula (I):

trihexyltetradecylphosphonium methanesulfonate;

tetrabutylphosphonium methanesulfonate;

tetraoctylphosphonium methanesulfonate;

tetrabutylphosphonium D-(+)-camphorsulfonate;

tetrapropylammonium methanesulfonate;

tetrabutylammonium methanesulfonate;

N-butylpyridinium methanesulfonate;

1-propyl-3-methylimidazolium methanesulfonate;

1-butyl-3-ethylimidazolium methanesulfonate;

1-hexyl-3-ethylimidazolium methanesulfonate;

1-butyl-3-ethylimidazolium methanesulfonate

1-butyl-3-ethylimidazolium DL-camphorsulfonate;

1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide;

N-hexyl-3-picolinium bis(trifluoromethanesulfonyl)imide;

tetrabutylphosphonium bis(trifluoromethanesulfonyl)imide; and

tetraoctylphosphonium bis(trifluoromethanesulfonyl)imide.

In general, the organic halide salt and alcohol or alkene or alkyne can be reacted in stoichiometric amounts, although the alcohol or alkene or alkyne may be present in excess, for example about 1.1 to about 12 equivalents relative to the organic halide salt. In particular, it will be preferred in some cases to use an excess alcohol or alkene or alkyne (for example between about 1.1 to about 12 equivalents, preferably about 2 to about 12 equivalents,

relative to the organic halide salt) to promote the conversion of halide ion to hydrocarbyl halide, so as to reduce the amount of halide ion that is present in the non-halide based ionic liquid product.

In general, the organic halide salt and the Bronsted acid can be reacted in stoichiometric amounts, although the Bronsted acid may be present in excess, for example about 1.01 to about 12 equivalents, preferably about 1.01 to about 1.3 equivalents, relative to the organic halide salt.

The reaction may be carried out by reacting organic halide salt with Bronsted acid and alcohol or alkene or aralkyne simultaneously. Alternatively, the reaction may be carried out in sequential steps: reacting organic halide salt Q^+X^- and Bronsted acid to obtain Q^+A^- and H^+X^-, then adding alcohol or alkene or aralkyne to convert H^+X^- to hydrocarbyl halide, and when alcohol is used, to hydrocarbyl halide and water.

The organic halide salt can be generated *in situ*, for example by reacting a hydrocarbyl halide with a reactant containing group Q, for example a tertiary nitrogen-based or tertiary phophorous-based compound (such as a tertiary amine, tertiary phosphine, imidazole, etc.), optionally in the presence of an alcohol, prior to the addition of the Bronsted acid.

In general, the reaction can be carried out over a wide range of temperatures, for example from between about 0°C to about 150°C, and pressures. The reaction is conveniently carried out at elevated temperatures, for example in the range of between about 100°C to about 150°C, and atmospheric pressure. Reaction times may range from

minutes to days, depending on conditions and particular reagents, but typically are on the order of 1 to 72 hours, more typically from about 2 to 24 hours.

Particularly in reactions where the Bronsted acid is a weak acid (such as a carboxylic acid, phosphonic acid or phosphinic acid), to facilitate formation of hydrocarbyl halide, it may be beneficial to add a small amount of a strong acid such as sulfuric acid. The strong acid is added in a small amount, for example in an amount ranging from about 0.001 equivalents to about 0.1 equivalents, preferably from about 0.001 equivalents to about 0.05 equivalents, more preferably from about 0.001 equivalents to about 0.01 equivalents, relative to the organic halide salt.

When the Bronsted acid is a carboxylic acid and an alcohol is present, formation of esters may compete with formation of hydrocarbyl halide. Formation of esters can be inhibited by adding water to the reaction mixture to shift the equilibrium of the esterification reaction to discourage formation of the esters. For example, water may be added in an amount ranging from about 0.01 equivalents to about 2 equivalents, preferably about 0.1 equivalents to about 1 equivalents, relative to organic halide salt.

The product Q^+A^- can be isolated by removing unreacted starting materials, hydrocarbyl halide and water, if present. Hydrocarbyl halide, unreacted starting materials, and water, if present, can be removed from the reaction mixture, for example by distillation, evaporation, extraction, or decantation. Distillation and evaporation are convenient methods for removing hydrocarbyl halides, unreacted starting materials, and water from the reaction mixture. Fractional distillation can be used to recover hydrocarbyl halide and unreacted alcohol or alkene.

Hydrocarbyl halide may also be removed by extraction, for example with hexane. Water and unreacted acid may be removed by distillation or evaporation, for example, under reduced pressure. In some cases, water may be removed by decantation.

The halide content of the product Q^+A^- can be assessed with $AgNO_3$ test or by electrochemical methods. If the halide content of the Q^+A^- is unacceptably high, it may be treated to reduce the amount of residual halide ion. The amount of halide ion in the product Q^+A^- can be reduced by adding to the product Q^+A^- a further quantity of alcohol or alkene or alkyne (under conditions similar to those described above) to convert residual halide ion to hydrocarbyl halide. The product Q^+A^- may then isolated by removing hydrocarbyl halide and water, if present, and unreacted starting materials by for example distillation. This procedure can be repeated as necessary to reduce the halide content of product Q^+A^-.

The product Q^+A^- obtained by the foregoing methods can be used directly or further purified, for example by dissolving it in a solvent (such as an alcohol, for example methanol, ethanol, propanol and isopropanol), mixing with activated carbon or charcoal, filtering, and removing solvent by for example evaporation under reduced pressure.

Hydrocarbyl halide removed from the reaction mixture can be recovered for use in chemical reactions. For example, recovered hydrocarbyl halide can be used for quaternization of imidazoles, pyridines, trialkylamines and trialkylphosphines to generate halide-based organic salts. If the halide-based organic salt is for use in generating a compound of formula (I) Q^+A^- according to the methods described herein, then it will be preferred that the solvent,

if present, for carrying out the quaternization reaction is an alcohol having a carbon backbone corresponding to that of the hydrocarbyl halide reagent.

Alcohol recovered from the reaction mixture can be recycled for use for example in subsequent chemical reactions, including but not limited to the current method for preparation of non-halide based ionic liquids.

The current invention is further illustrated by way of the following non-limiting examples.

Example 1: Preparation of trihexyltetradecylphosphonium methanesulfonate:

To a 125 ml two-neck round-bottom flask mounted with a 30 cm fractional distillation column were added trihexyltetradecylphosphonium chloride (51.8 g, 0.1 mol) and methanesulfonic acid (redistilled, 9.61 g, 0.1 mol). Ethanol (2 equivalent, redistilled) was added into the mixture. The mixture was heated to 100°C using an oil bath, and chloroethane was removed from the reaction mixture by distillation under ambient pressure. Water and ethanol were removed by evaporation under reduced pressure.

A further 2 eq. of ethanol was added to the reaction vessel. The reaction vessel was heated to 100°. Chloroethane was again removed via distillation. Water and ethanol were again removed via evaporation under reduced pressure. The foregoing process was repeated once more using another equivalent of ethanol.

Trihexyltetradecylphosphonium methanesulfonate ionic liquid product (colorless) was obtained in approximately 100% yield at approximately 100% purity, as confirmed by Nuclear Magnetic Resonance (NMR). No

precipitate was observed when the ionic liquid was tested for the presence of chloride using 10% aqueous $AgNO_3$.

Example 2: Preparation of tetrabutylphosphonium methanesulfonate:

Tetrabutylphosphonium methanesulfonate was prepared using the method described in Example 1, except that tetrabutylphosphonium bromide (33.9 g, 0.1 mol), methanesulfonic acid (redistilled, 9.61 g, 0.1 mol) and ethanol (5 equivalent, redistilled) were used.

Tetrabutylphosphonium methanesulfonate was obtained in approximately 100% yield at approximately 100% purity, as confirmed by NMR.

Example 3: Preparation of tetraoctylphosphonium methanesulfonate:

Tetraoctylphosphonium methanesulfonate was prepared using the method described in Example 1, except that tetraoctylphosphonium bromide (56.3 g, 0.1 mol), methanesulfonic acid (redistilled, 9.61 g, 0.1 mol) and ethanol (5 equivalent, redistilled) were used.

Tetraoctylphosphonium methanesulfonate was obtained in approximately 100% yield at approximately 100% purity, as confirmed by NMR.

Example 4: Preparation of tetrabutylphosphonium D-(+)-camphorsulfonate:

Tetrabutylphosphonium D-(+)-camphorsulfonate was prepared using the method described in Example 1, except that D-(+)-camphorsulfonic acid (9.3 g, 0.04 mol) and ethanol (5 equivalent, redistilled) were used.

Tetrabutylphosphonium D-(+)-camphorsulfonate was obtained in approximately 100% yield at approximately 100% purity, as confirmed by NMR.

Example 5: Preparation of tetrapropylammonium methanesulfonate:

Tetrapropylphosphonium methanesulfonate was prepared using the method described in Example 1, except that tetrapropylammonium bromide (26.6 g, 0.1 mol), methanesulfonic acid (redistilled, 9.61 g, 0.1 mol) and ethanol (6 equivalent, redistilled) were used.

Tetrapropylphosphonium methanesulfonate was obtained in approximately 100% yield at approximately 100% purity, as confirmed by NMR.

Example 6: Preparation of tetrabutylammonium methanesulfonate:

Tetrabutylammonium methanesulfonate was prepared using the method described in Example 1, except that tetrabutylammonium bromide (32.2 g, 0.1 mol), methanesulfonic acid (redistilled, 9.61 g, 0.1 mol) and ethanol (7 equivalent, redistilled) were used.

Tetrabutylammonium methanesulfonate was obtained in approximately 100% yield at approximately 100% purity, as confirmed by NMR.

Example 7: Preparation of *N*-butylpyridinium methanesulfonate:

N-butylpyridinium methanesulfonate was prepared using the method described in Example 1, except that *N*-butylpyridinium bromide (21.6 g, 0.1 mol), methanesulfonic acid (redistilled, 9.61 g, 0.1 mol) and ethanol (3 equivalent, redistilled) were used.

N-butylpyridinium methanesulfonate was obtained in approximately 100% yield at approximately 100% purity, as confirmed by NMR.

Example 8: Preparation of 1-propyl-3-methylimidazolium methanesulfonate:

1-propyl-3-methylimidazolium methanesulfonate was prepared using the method described in Example 1, except that 1-propyl-3-methylimidazolium bromide (65.6 g, 0.32 mol), methanesulfonic acid (redistilled, 30.8 g, 0.32 mol) and propanol (5 equivalent, redistilled) were used.

1-propyl-3-methylimidazolium methanesulfonate was obtained in approximately 100% yield at approximately 100% purity, as confirmed by NMR.

Example 9: Preparation of 1-butyl-3-ethylimidazolium methanesulfonate:

1-butyl-3-ethylimidazolium methanesulfonate was prepared using the method described in Example 1, except that 1-butyl-3-ethylimidazolium bromide (23.3 g, 0.1 mol), methanesulfonic acid (redistilled, 9.61 g, 0.1 mol) and ethanol (6 equivalent, redistilled) were used.

1-butyl-3-ethylimidazolium methanesulfonate was obtained in approximately 100% yield at approximately 100% purity, as confirmed by NMR.

Example 10: Preparation of 1-hexyl-3-ethylimidazolium methanesulfonate:

1-hexyl-3-ethylimidazolium methanesulfonate was prepared using the method described in Example 1, except that 1-hexyl-3-ethylimidazolium bromide (27.3 g, 0.1 mol),

methanesulfonic acid (redistilled, 9.61 g, 0.1 mol) and ethanol (4 equivalent, redistilled) were used.

1-hexyl-3-ethylimidazolium methanesulfonate was obtained in approximately 100% yield at approximately 100% purity, as confirmed by NMR.

Example 11: Preparation of 1-butyl-3-ethylimidazolium DL-camphorsulfonate:

1-butyl-3-ethylimidazolium DL-camphorsulfonate was prepared using the method described in Example 1, except that 1-butyl-3-ethylimidazolium bromide (46.6 g, 0.2 mol), DL-camphorsulfonic acid (46.5 g, 0.2 mol) and ethanol (7 equivalent, redistilled) were used.

1-butyl-3-ethylimidazolium DL-camphorsulfonate was obtained in approximately 100% yield at approximately 100% purity, as confirmed by NMR.

Experiment 12: Purification of ionic liquid products using activated charcoal:

A 250 ml round-bottom flask was charged with 50 ml of 1-butyl-3-ethylimidazolium methanesulfonate (brownish) obtained in Example 9, 50 ml of ethanol and 20 g of charcoal (4-20 mesh). The mixture was heated to 50°C and maintained at this temperature overnight, with stirring. The reaction mixture was filtered and the filtrate was concentrated by evaporation under reduced pressure to remove ethanol.

The 1-butyl-3-ethylimidazolium methanesulfonate (slightly yellowish) was obtained in approximately 100% yield at approximately 100% purity, as confirmed by NMR.

Example 13: Preparation of tetrabutylphosphonium bis(trifluoromethanesulfonyl)imide:

To a 4 dram vial was added tetrabutylphosphonium bromide (a 71.2% solution in 28.8% of isopropanol, a Cytec compound CYPHOS 442P; 1.62 g, 0.0034 mol) and bis(trifluoromethanesulfonyl)imide (0.96 g, 0.0034 mol) at room temperature with stirring. The mixture was heated using an oil bath (95°C) to allow 2-bromopropane to evaporate. $AgNO_3$ test showed absence of bromide anion. Another portion of isopropanol (0.5 ml, 0.0065 mol) was added to the mixture and heating was continued overnight to evaporate all volatiles. Tetrabutylphosphonium bis(trifluoromoethanesulfonyl)imide was obtained in approximately 100% yield at approximately 100% purity, as comfirmed by NMR.

Example 14: Preparation of tetraoctylphosphonium bis(trifluoromethanesulfonyl)imide:

To a 4 dram vial was added tetraoctylphosphonium bromide (a Cytec compound CYPHOS 482; 1.69 g, 0.003 mol), 1-propanol (0.732 g, 0.012 mol) and bis(trifluoromethanesulfonyl)imide (0.9 g, 0.0031 mol) at room temperature with stirring. The mixture was heated using an oil bath (95°C) to allow 1-bromopropane to evaporate. $AgNO_3$ test showed absence of bromide anion. Another portion of 1-propanol (0.5 ml, 0.0067 mol) was added to the mixture and heating was continued overnight to evaporate all volatiles. Tetraoctylphosphonium bis(trifluoromoethanesulfonyl)imide was obtained in approximately 100% yield at approximately 100% purity, as comfirmed by NMR.

Example 15: Preparation of tetraoctylphosphonium bis(trifluoromethanesulfonyl)imide:

To a 4 dram vial was added tetraoctylphosphonium bromide (a Cytec compound CYPHOS 482; 1.76 g, 0.0031 mol) and bis(trifluoromethanesulfonyl)imide (0.9 g, 0.0031 mol) at room temperature with stirring. A stream or propene was bubbled into the slightly reddish liquefied mixture for 4 hours. NMR showed the formation of 2-bromopropane. All volatiles were then evaporated off on a rotavapor. $AgNO_3$ test showed absence of bromide anion. Tetraoctylphosphonium bis(trifluoromoethanesulfonyl)imide was obtained in approximately 100% yield at approximately 100% purity, as comfirmed by NMR.

Example 16: Preparation of 1-butyl-3-methylimidazolium bromide in ethanol:

To a 250 ml flat bottom flask immersed in an ice-bath was added 1-bromobutane (249 g, 1.82 mol), ethanol (70 g, 1.52 mol) and 1-methylimidazole (redistilled, 124.5 g, 1.52 mol). The mixture was stirred for 72 hr to provide a colorless liquid. NMR showed that no 1-methylimidazole remained in the reaction mixture.

Example 17: Preparation of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide:

A mixture of 1-butyl-3-methylimidazolium bromide (0.267 g, 1.22 mmol), methanol (0.047 g, 1.44 mmol) and bis(trifluoromethanesulfonyl)imide (0.372 g, 1.32 mmol) sealed in a vial was stirred at room temperature then heated to 50°C overnight with stirring. The progress of the reaction was followed with NMR and Mass Spectrophotometry (MS). When the reaction was completed, volatiles were removed by evaporation under reduced pressure. The contents

of the flask were then dried to remove water under reduced pressure at 60°C.

1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (a colorless liquid) was obtained in approximately 100% yield (0.513 g) at approximately 100% purity as assessed by NMR and MS.

Example 18: Preparation of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide:

A mixture of 1-butyl-3-methylimidazolium bromide (0.228 g, 1.05 mmol), isopropanol (0.075 g, 1.26 mmol) and bis(trifluoromethanesulfonyl)imide (0.322 g, 1.15 mmol) was sealed in a vial was stirred at room temperature for about 4 hours, then heated to 50°C overnight with stirring. The reaction was followed by NMR and MS. When the reaction was complete, the reaction mixture was worked up by evaporating off volatile compounds under reduced pressure. The reaction mixture was then dried to remove water under reduced pressure at 60°C.

The product, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, was obtained as a colorless liquid in approximately 100% yield (0.438 g) at approximately 100% purity as determined by NMR and MS.

Example 19. Preparation of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide:

A mixture of 1-butyl-3-methylimidazolium bromide (0.285 g, 1.31 mmol), *t*-butanol (0.116 g, 1.56 mmol) and bis(trifluoromethanesulfonyl)imide (0.323 g, 1.44 mmol) was sealed in a vial was stirred at room temperature for 4 hours, then heated to 50°C overnight with stirring. The reaction was followed by NMR and MS. When the reaction was completed,

volatile compouds were removed from the reaction by evaporation under reduced pressure. The reaction mixture was further dried to remove water by evaporation under reduced pressure at 60°C.

The product, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, was obtained as a colorless liquid in approximately 100% yield (0.547 g) at approximately 100% purity as determined by NMR and MS.

Example 20. Preparation of N-hexyl-3-picolinium bis(trifluoromethanesulfonyl)imide:

A mixture of N-hexyl-3-picolinium bromide (0.216 g, 0.84 mmol), isopropanol (0.082 g, 1.36 mmol) and bis(trifluoromethanesulfonyl)imide (0.257 g, 0.92 mmol) was sealed in a vial and stirred at room temperature for 1 hour, then heated to 50°C overnight with stirring. The reaction was followed by NMR and MS. When the reaction was completed, volatile compounds were removed by evaporation under reduced pressure. The reaciton mixture was further dried to remove water under reduced pressure at 60°C.

The product, N-hexyl-3-picolinium bis(trifluoromethanesulfonyl)imide, was a pale-yellow liquid obtained in approximately 100% yield (0.383 g) and approximately 100% purity as determined by NMR and MS.

Example 21. Preparation of N-hexyl-3-picolinium bis(trifluoromethanesulfonyl)imide:

A mixture of N-hexyl-3-picolinium bromide (0.223 g, 0.86 mmol), *t*-butanol (0.077 g, 1.04 mmol) and bis(trifluoromethanesulfonyl)imide (0.265 g, 0.94 mmol) sealed in a vial was stirred at room temperature for 1 hour, then heated to 50°C overnight with stirring. The reaction

was followed by NMR and MS. When the reaction was completed, volatile compounds were removed from the reaction mixture by evaporation under reduced pressure. The reaction mixture was further dried to remove water under reduced pressure at 60°C.

The product, N-hexyl-3-picolinium bis(trifluoromethanesulfonyl)imide, was a pale-yellow liquid obtained in approximately 100% yield (0.395 g) and approximately 100% purity as determined by NMR and MS.

CLAIMS:

1. A method for preparing a compound of formula (I) Q^+A^-, the method comprising reacting:

(i) an organic halide salt of formula (II) Q^+X^-, wherein

Q^+ is an organic cation and

X^- is a halide;

with

(ii) a Bronsted acid other than a hydrohalic acid, wherein said Bronsted acid has a conjugate base A^-; and

(iii) an alcohol or an alkene or an alkyne;

with the proviso that when Q^+ is 1-butyl-3-methylimidazolium, HA is not H_2SO_4 or CH_3SO_3H.

2. The method of claim 1, wherein hydrocarbyl halide is removed from the reaction mixture by distillation or evaporation.

3. The method of claim 2, further comprising, after the distillation or evaporation, adding to the reaction mixture a further quantity of alcohol or alkene or alkyne, and removing by distillation or evaporation hydrocarbyl halide.

4. The method of any one of claims 1 to 3, wherein product Q^+A^- is isolated by removing unreacted starting materials, hydrocarbyl halide, and water if present, by distillation or evaporation.

5. The method of any one of claims 1 to 4, wherein the reaction temperature is between about 0°C and about 150°C.

6. The method of claim 5, wherein the temperature is from between about 100°C and about 150°C.

7. The method of any one of claims 1 to 6, wherein the alcohol is present in excess relative to the organic halide salt.

8. The method of claim 7, wherein the alcohol is present in a range between about 1.2 to about 12 equivalents relative to the organic halide salt.

9. The method of claim 8, wherein the alcohol is present in a range between about 2 to about 12 equivalents relative to the organic halide salt.

10. The method of any one of claims 7 to 9, wherein the alcohol is selected from the group consisting of: methanol, ethanol, n-propanol, iso-propanol, n-butanol, sec-butanol, tert-butanol, pentanol, hexanol, heptanol, octanol, nonanol, and decanol.

11. The method of any one of claims 1 to 6, wherein the alkene is present in excess relative to the organic halide salt.

12. The method of claim 11, wherein the alkene is present in a range between about 1.2 to about 12 equivalents relative to the organic halide salt.

13. The method of claim 12, wherein the alkene is present in a range of between about 2 to about 12 equivalents relative to the organic halide salt.

14. The method of any one of claims 11 to 13, wherein the alkene is selected from the group consisting of propene, butene, hexene, cyclopentene, and cyclohexene.

15. The method of any one of claims 1 to 6, wherein the Bronsted acid is a weak acid selected from the group consisting of carboxylic acids, phosphonic acids, and phosphinic acids, and a strong acid is added to the reaction mixture to facilitate formation of alkyl halide.

16. The method of claim 15, wherein the strong acid is added in an amount ranging from about 0.001 equivalents to about 0.1 equivalents relative to the organic halide salt.

17. The method of claim 15, wherein the strong acid is added in an amount ranging from about 0.001 equivalents to about 0.05 equivalents relative to the organic halide salt.

18. The method of claim 15, wherein the strong acid is added in an amount ranging from about 0.001 equivalents to about 0.01 equivalents relative to the organic halide salt.

19. The method of any one of claims 1 to 18, wherein the organic halide salt is selected from the group consisting of: ammonium salts, phosphonium salts, pyridinium salts, imidazolium salts, pyrazolium salts, pyrimidinium salts, pyridazinium salts, pyrazinium salts, 1,2,3-triazolium salts, 1,2,4-triazolium salts, tetrazolium salts and isothiazolium salts.

20. The method of claim 19, wherein the organic halide salt is selected from the group consisting of:

trihexyltetradecylphosphonium chloride;

tetrabutylphosphonium bromide;

tetraoctylphosphonium bromide;

tetrapropylammonium bromide;

tetrabutylammonium bromide;

N-butylpyridinium bromide;

1-propyl-3-methylimidazolium bromide;

1-butyl-3-ethylimidazolium bromide;

1-hexyl-3-ethylimidazolium bromide;

1-butyl-3-ethylimidazolium chloride; and

N-hexyl-3-picolinium bromide.

21. The method of any one of claims 1 to 14, wherein:

(a) Q^+ is selected from the group consisting of: ammonium, phosphonium, pyridinium, imidazolium, pyrazolium, pyrimidinium, pyridazinium, pyrazinium, 1,2,3-triazolium, 1,2,4-triazolium, tetrazolium, and isothiazolium; wherein Q^+ has at least one hydrocarbyl group consisting of a C_1-C_{30} alkyl, C_1-C_{30} alkyloxy, C_3-C_7 cycloalkyl, C_3-C_7 cycloalkyloxy, C_6-C_{18} aryl, C_6-C_{18} aryloxy, C_7-C_{30} aralkyl, or C_7-C_{30} aralkyloxy, substituted or unsubstituted and optionally containing one or more heteroatoms; and

(b) the Bronsted acid has a conjugate base selected from the group consisting of: RSO_3^-, camphorsulfonates, RSO_2^-, RSO_4^-, $H_2PO_4^-$, $H_2PO_3^-$, $(RO)_2P(O)O^-$, $(R)P(O)(OH)O^-$, $(R)_2P(O)O^-$, carboxylates, NO_3^-, NO_2^-, ClO_4^-, phenolates, $HCrO_4^-$, $H_2AsO_4^-$, $H_2AsO_3^-$, $HSeO_3^-$, $HTeO_6^-$, and $HTeO_3^-$, and when Q^+ has a quaternary phosphorus atom or a quaternary nitrogen atom also $(RSO_2)_2N^-$, wherein R is hydrogen or C_1-C_{30} alkyl, C_2-C_{30} alkenyl, C_2-C_{30} alkenyl, C_3-C_7 cycloalkyl, C_3-C_7 cycloalkenyl, C_6-C_{18} aryl, C_7-C_{30} aralkyl, C_8-C_{30} aralkenyl, or C_8-C_{30} aralkynyl, substituted or unsubstituted and optionally containing one or more heteroatoms selected from the group consisting of oxygen, nitrogen, sulfur and silicon.

22. The method of claim 21, wherein R is substituted with one or more substituents selected from the group consisting of alkoxy, alkylthio, acetyl, and halogen atoms.

23. The method of claim 21, wherein R is substituted with one or more fluorine atoms.

24. The method of any one of claims 1 to 6, wherein the Bronsted acid is a carboxylic acid and alcohol is present, and water is added to inhibit formation of esters.

25. The method of claim 24, wherein water is added in an amount ranging from about 0.01 equivalents to about 2 equivalent, relative to organic halide salt.

26. The method of claim 24, wherein water is added in an amount ranging from about 0.1 equivalents to about 1 equivalent, relative to organic halide salt.

27. The method of any one of claims 1 to 26, wherein the compound of formula (I) Q^+A^- is substantially free of halide.

28. The method of any one of claims 1 to 18 or 24 to 27, wherein the compound of formula (I) Q^+A^- is selected from the group consisting of:

trihexyltetradecylphosphonium methanesulfonate;

tetrabutylphosphonium methanesulfonate;

tetraoctylphosphonium methanesulfonate;

tetrabutylphosphonium D-(+)-camphorsulfonate;

tetrapropylammonium methanesulfonate;

tetrabutylammonium methanesulfonate;

N-butylpyridinium methanesulfonate;

1-propyl-3-methylimidazolium methanesulfonate;

1-butyl-3-ethylimidazolium methanesulfonate;

1-hexyl-3-ethylimidazolium methanesulfonate;

1-butyl-3-ethylimidazolium methanesulfonate

1-butyl-3-ethylimidazolium DL-camphorsulfonate;

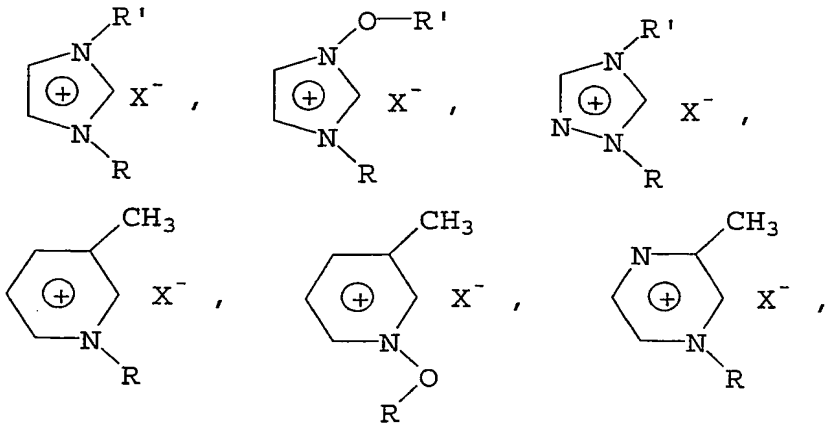
1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide;

N-hexyl-3-picolinium bis(trifluoromethanesulfonyl)imide;

tetrabutylphosphonium bis(trifluoromethanesulfonyl)imide; and

tetraoctylphosphonium bis(trifluoromethanesulfonyl)imide.

29. The method of any one of claims 1 to 18 or 24 to 27, wherein the compound of formula (I) Q^+A^- is a compound according to one of the following formulae:



$(R)_4N^+X^-$ and $(R)_4P^+X^-$,

wherein R and R′ are alkyl radicals with 1 to 12 carbon atoms, and

X- is $(CF_3SO_2)_2N^-$, $CF_3(CF_2)_2CO_2^-$, $CF_3(CF_2)_3SO_3^-$, $CH_3SO_3^-$, HSO_4^-, or $H_2PO_4^-$.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 00 16902 A (KEIM WILLI ;KORTH WOLFGANG (DE); WASSERSCHEID PETER (DE); BP CHEM) 30 March 2000 (2000-03-30) page 10, line 5 - line 15	1-29
A	US 4 048 141 A (CORNELL III MARTIN C ET AL) 13 September 1977 (1977-09-13) example 22	1-29

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Kollmannsberger, M

Form PCT/ISA/210 (second sheet) (July 1992)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PREPARATION OF IONIC LIQUIDS

(57) Abstract: Provided is a method for preparation of non-halide based ionic liquids, comprising reacting a halide salt of an organic cation with a Bronsted acid in the presence of an alcohol or alkene or alkyne. The non-halide based ionic liquid product of the reaction can be purified by removing hydrocarbyl halide, and any unreacted starting materials and water if present, for example by distillation. The halide ion content of the ionic liquid product can be minimized by using an excess of alcohol or alkene or alkyne in the reaction and/or treating crude ionic liquid with a further quantity of alcohol or alkene or alkyne.

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